

ERYTHRITOL TETRANITRATE

Lab Notes:4/3/06

Please note that I started off copying a method found already tested.

Reactants used:

100ml (178g) H₂SO₄ (93%) (I have found that SOME H₂SO₄ is higher % than others. I would digress and say that brands such as Roto are 93 while others may be in the 95-6 range. Remember this is surplus acid from various sources.)

61g NH₄NO₃ (VERY finely powdered)

20g C₄-H₁₀-O₄ (Erythritol)

2000ml H₂O ESU (Estimated Substance Used)

200g NaHCO₃ ESU (Estimated Substance Used)

Equation:

H₂SO₄ + NH₄NO₃ --> HNO₃ + NH₄HSO₄? (Not Sure)

C₄H₁₀O₄ + 4HNO₃ --> C₄H₆N₄O₁₂ + 4H₂O

g (44.44ml) H₂SO₄ + 60g NH₄NO₃ --> 40g (28.57ml) HNO₃ + 73.23g NH₄HSO₄? (I would need a bit more H₂SO₄ since it's not concentrated therefore 50ml is good.)

19.52g C₄-H₁₀-O₄ + 40g (28.57 ml) HNO₃ --> 48.32g C₄H₆N₄O₁₂ + 11.52g H₂O

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04/10/06

---->This is the best one:

20gr Erythritol

60gr ammonium nitrate

110ml H₂SO₄ (93%)

Mix the solid nitrate and acid w/ magnetic stirring device until clear solution is formed; cover with Al foil. Refrigerate. Maintain @ 20C. When COLD use ice/water bath to maintain temp and add Erythritol about ½ gram at a time.

Solution will thicken quickly. Continue to stir w/ hand stirring. Then

refrigerate one hour. Yield will be approx 85% or about 40gr ETN !

Re-crystallize with etoh. Acetone is too soluble but both will suffice. Re-crystallization is a major issue. What has proven itself is 1/4 acetone - 3/4 etoh. Methanol does not appear to be a useful solvent. Too strong is acetone;

dissolving Erythritol Tetranitrate to an extreme. When used in moderation it

will help the re-crystallization but will add a yellow when heat is applied.

Pure ethanol appears to be best but it takes a great deal of solvent to totally dissolve the raw material. the object is to dissolve the raw Erythritol

Tetranitrate and then re-crystallize it without any acid in the crystal and with

some stabilizer such as dimethelamine. Unlike PETN, Erythritol Tetranitrate is

not as stable and needs the attention given MHN or other powdered nitric esters.

Performance wise it is on par with NG, PETN, or MHN; about 7000mps but it will

not match PETN for overall stability. It is close, if given proper re-

crystallization and stabilization. Far easier to make properly than MHN and it's

raw material much more readily available than PETN. A quick test of placing a

few milligrams on a steel anvil and striking it with a hammer will demonstrate

it's success and, of course, it's power. A bit the size of a match-head folded

in some foil and hit with a hammer will detonate with all the volume of a small

caliber pistol.

NOTE: I used differing weights of NH₄NO₃ and excess sulfuric acid; This had been altered from the original percentages of this synch. The same goes with the extra Erythritol, To improve yields should more nitric be produced, I lowered the original weights (from 25 to 20 gr of Erythritol.

4/10 Procedure:

H₂SO₄ was chilled inside of a flask, in the freezer. After taking it out, the procedure followed immediately. The chilled H₂SO₄ was measured out to be -10

degrees C. The flask was placed magnetic stir platform. NH₄NO₃ was added in

small portions, not letting the temperature jump higher than 15 degrees C. After

the full addition of the NH₄NO₃ I pulled out thermometer and noticed white

fumes, signifying that I had high % nitric, the addition of C₄-H₁₀-O₄ (aka E)

began. The E was added slowly again not letting the temp jump over 15 degrees C

to reduce loss of possible nitric loss. The mixture was white with some NH₄NO₃

left over in it, but it dissolved after the addition of E. The flask was

measured at 5 degrees C right before E addition. The mix was left to nitrate for 55 minutes with stirring ever 5 minutes or so. The mix was thick and creamy. This was dumped into a 400ml flask with water. The mix immediately became cloudy, signs of a decent yield. This mixed solution was then poured SLOWLY into a beaker of cold ice water. I was sure to wash the material with a solution of baking soda repeatedly as I do not attempt to reutilize at the time of nitration but always re-crystallize and at that time use other neutralization methods & diphenylamine for stabilization. I added some more NaHCO_3 to test for complete neutralization (none occurred.) This was again dumped into water for removal of any water-soluble stuffs. The ETN was then filtered through a large paper towel. Drying was done in the free air on top of dry paper towels. There were some problems though because the pot that held my filter was not big enough so I had to do 3 filtrations, one of them worked very well with at least 15g of product. The second one failed and my "neutralized mixture" ate right through the 3 paper towels I was using for filtering. It had an estimated 15g on it. The third was a re-filtration of the second and I got around 5-10g on it. The two filtered products are drying. My 1st attempt w/ KNO_3 was not nearly as good as the NH_4NO_3 . I made sure of not only the weight but ground it further in a coffee mill. This produced a ultra fine powder that mixed very well. However it is to be noted that even w/ a magnetic stir plate after a bit the mix was too heavy to mix without a manual method.

Estimated (before filtration Yield): 35+g of ETN
Estimated (after filtration) Yield: 25g of ETN
Actual Yield: 50 grams of ETN
at least 90% Efficiency ?

Note some stuff isn't filled in, this is because it's still drying I will edit that in later. Here are some things I learned:

NOTES: Recrystallization issues

DATE: 4/12/06

The need for re-crystallization is undisputed. What was a question was if another stabilizer besides dimethylamine is effective. DMA has been used commercially with nitric esters for decades. Would another stabilizer produce results similar? My options were betaine & Urea. The use of either introduced impurities as my sources were not reagent to begin with. What became necessary was to re-crystallize twice. The initial re-crystallization produced a product that was off white in colour. Using the above "4/10 procedure" a yield of well over 85% was easy time and again. The 4/10 procedure was scaled up 100% to a 40 gram Erythritol starting point. The dry weights were fantastic but the colour was a question. Notice the copper penny against the white background to understand hue (and bulk) of dry product. Understand that this is coarse, grainy crystals. Not light and fluffy in any way. Similar in texture to rough raw sugar. An EXCELLENT yield!



Although out of focus the colour indicates some need for refinement. What was used for a simple impact test was a 3-5 mg amount placed inside of a fold of Al foil and struck with a falling hammer on a steel anvil. The report was shattering. Indicating a well nitrated product. ETN is very impact sensitive. I believe it is well more sensitive than PETN but its initiation properties may be somewhat less (DuPont, 1931). This was exposed to a warm environment for a protracted period of days in an enclosure with a DMA patch used as a blue indicator for nitrate loss. It appeared stable for 14 days @ 60C. It appeared stable for 6 days @ 75 C.



Same material (ETN) after protracted temp exposure. Product appears stable and maintains the same sensitivity. 3 - 5 mg when allowed a hammer fall (1.5 hammer) produced the same results. Seemingly no more or less.

Weight for a 40 grams batch of Erythritol was 62.5 grams of ETN using the 4/10 procedure. After exposure to temp testing the weight was the same. (+ or - .001 gram). Care was maintained to use dry crystals to begin testing / measurement, etc.

There are some important issues to remember - The nitrating acid was totally mixed in a covered beaker until completely clear and then chilled to 0 C to begin with. Thus the nitration was the dynamic that brought the material up to 20 C as the Erythritol was added. The Erythritol was added at .5 gr at a time every 60 seconds during nitration. This whole set of experiments was held under lab conditions with a magnetic stirring device in a salt / ice bath. After the whole of the Erythritol was added the material was then chilled for 2 hours prior to drowning. The drowning was the point wherein the Urea was added to the drowning solution. With Urea it was mixed with the drown water. If DMA was used it was mixed with ethyl acetate and that was added to the drown as it was miscible with water. However etoh could be substituted as could acetone which is also miscible with water.

Re-crystallization is perhaps one of the most important issues to the stability of a solid nitrated material. With ETN acetone, Ethyl alcohol and methanol may be used. Acetone is just too strong of a solvent. The acetone that is available OTC is too impure to provide results that are not impaired by extraneous

material in the final product. Acetone re-crystallization is not a productive effort. Mixing OTC (technical-industrial grade) acetone with alcohols adds hydrocarbons to the final product. Alcohols appear to be the best solvent. When a comparison of etoh to methanol is made the results appear to be in crystal shape. Ethyl appears to make for platelets and some tiny needles but the variance is wide. Comparison is made under a microscope @ 100x. methanol shows more consistency and the crystals show a density not seen with ethanol. Both provide crystals that are easily shaved in handling to the point of 1.6 - 1.8 gr / cc density levels. Higher density could easily be achieved via shaving. Below is a double re-crystallization. That is the final product has been re-crystallized twice; bringing about an almost clear crystal whose density is fractionally higher and response is the same to that which has been re-crystallized once. It appears to be of near total purity.



Loss level was .75 grams which may be completely appropriate to the impurities contained in the original material. Unfortunately the photographs are poor but the pictured material is coarse and dense. During the experiments many pictures were taken of the material at differing stages of it's refinement. A note of interest is that the response to impact stimuli did not change during it's refinement. However when tested for decomposition at it's final stages it seems that the higher levels of purity allow it to maintain it's stability at longer levels of temp variance exposure. Final test results indicate that the "white" product that had been re-crystallized twice would withstand temps of 75 C + for a period of weeks. A far greater exposure level than would occur in normal handling of this product.



The following pages are US patents 1691954 (original production ETN Frank Bergeim's work in 1928) and US patent 1744693 (DuPont's pirate piece). I can have studied these for quite awhile and believe that the only reason that ETN did not find a stronger place in history is the price of Erythritol due to production methods of that era placed it out of reach for industry to capitalize on what is essentially a more sensitive and more reactive PETN. ETN's reaction to electrical stimuli may make it a material of choice for a secondary only det cap. Or an impact primer for small arms, etc, etc.

Patented Nov. 20, 1928.

1,691,954

UNITED STATES PATENT OFFICE.

FRANK H. BERGEIM, OF WOODBURY, NEW JERSEY, ASSIGNOR TO E. I. DU PONT DE NEMOURS & COMPANY, OF WILMINGTON, DELAWARE, A CORPORATION OF DELAWARE.

PRODUCTION OF ERYTHRITOL TETRANITRATE.

No Drawing.

Application filed April 15, 1927. Serial No. 184,180.

This invention relates to the production of erythritol tetranitrate, and more particularly relates to the nitration of erythritol, $C_4H_8(OH)_4$, by dissolving the same in sulphuric acid and adding the solution to nitric acid or mixed acid containing a large proportion of nitric acid. Also the invention relates to the stabilization of erythritol tetranitrate. The major objects of the invention are to provide such procedures.

In the literature (Stenhouse Ann. 70, 226) it is reported that erythritol tetranitrate may be prepared by dissolving erythritol in strong nitric acid and precipitating the nitrated product by adding sulphuric acid. However, the product prepared by this method has a poor chemical stability (Naoum, Nitroglycerine and Nitroglycerine Sprengstoffe p. 218). In addition to the undesirable chemical stability of the product thus prepared the process itself is open to serious objection as being unsafe for commercial manufacture, in that it involves the dissolution of an organic body in strong nitric acid, forming a mixture in itself an explosive. I have provided a process, comprised by the present invention, wherein are embodied new and valuable features, making the process itself safe as a manufacturing operation and producing a product markedly superior in chemical stability to that previously prepared.

The safety feature involves, as the first step, the dissolving of erythritol in sulphuric acid. This liberates considerable heat of reaction in forming a non-explosive compound, thus preventing this heat from being liberated later in the process when erythritol comes in contact with nitric acid. When the sulphuric acid solution is added to strong nitric acid or a mixed acid high in nitric acid, so little heat is liberated that the nitrator must even be kept warm with steam.

Another feature of the present process is the stabilization of the nitrated product by dissolving it in a water soluble solvent such as alcohol or acetone, adding a weak alkali such as sodium or ammonium carbonate, and then forcing the erythritol tetranitrate out of solution by adding water. This method of stabilization gives a product of excellent stability superior in this respect to the erythritol tetranitrate described in the literature.

Without restricting the invention thereto, the following is cited as a specific example of the manner in which the invention may be

carried out (parts by weight):—One part of erythritol is dissolved in $5\frac{1}{2}$ parts of concentrated sulphuric acid 90-95% strength, using cooling water to prevent the temperature rising to such an extent that the erythritol becomes carbonized, it being advisable not to permit the temperature to rise above 40 to 50° C. When all of the erythritol has dissolved this solution is run into 7 parts of strong nitric acid (90-100%) keeping the temperature between 40° and 60° C. Instead of strong nitric acid, there may be used with equally good results a mixed acid of relatively low sulphuric acid content, containing for example 12% H_2SO_4 , 80% HNO_3 , and 8% H_2O . The mixture is then agitated for a short time, say 20 to 30 minutes, after the addition of the sulphuric acid solution has been completed. The erythritol tetranitrate separates as an oil in the warm waste acid. By cooling slowly with rapid agitation the explosive is obtained in a fine crystalline condition. It may be filtered from the waste acid, or the whole mixture drowned. In either case, the slightly acid product is purified and stabilized by dissolving in warm alcohol, treating the alcoholic solution with preferably powdered ammonium carbonate until neutralized, and cooling to crystallize. Desirably, the neutralized product may be forced out of solution by adding water. The explosive thus obtained is a white crystalline product having excellent stability and a nitrogen content very close to the theoretical (18.53% N).

In the method of stabilization, it is to be understood that other water soluble solvents than alcohol may be used. It is not necessary to add water to the solvent in order to obtain a satisfactory product but by so doing the yield is brought up to very near the theoretical. It is also to be understood that other weak alkalies than ammonium carbonate, such as sodium and potassium carbonates or bicarbonates may be used; and in the claims references to "carbonate" are to be understood as including "bicarbonate", except as otherwise evident. Furthermore, while the preferred process of stabilizing comprises dissolving the crude product in a water soluble solvent, e. g. alcohol, and (after neutralizing) forcing the product out of solution by adding water, since water soluble solvents offer the advantage of dissolving an appreciable amount of carbonate and also offer the advantage of giving the opportunity of completely recovering the

stabilized product by subsequent mixing with water, it is to be understood that water soluble solvents need not necessarily be used. Thus, solvents such as chloroform, ether and
5 toluene may be used; but recovery of the stabilized product from these solutions is more difficult and expensive than from water-soluble solvents. Whether water-soluble, or water-insoluble solvents be used and whether or
10 not forcing the product out by the addition of water be resorted to, a particular feature of the stabilization procedure is, the treatment of erythritol tetranitrate in solution with weak alkali.
15 In regard to the nitration process proper, it is not necessary to adhere strictly to the acid ratios given in order to obtain goods results. While I prefer the ratio of $5\frac{1}{2}$ parts of sulphuric acid to one of erythritol, an equally
20 good product, though in smaller yield, may be obtained by increasing or decreasing this ra-

tio. In the same way, the nitric acid or mixed acid ratios may be varied widely without departing from the spirit of the invention.

I claim:

1. A process for the nitration of erythritol which comprises dissolving the alcohol in sulphuric acid, and adding the solution thus prepared to nitric acid. 25
2. The process of claim 1 in which the sulphuric acid is of 90-95% strength. 30
3. The process of claim 1 in which the nitric acid contains sulphuric acid.
4. The process of claim 1 in which the nitric acid is of about 90% strength. 35
5. The process of claim 1 in which the temperature of the nitrating mixture is maintained at about 40-60° C. until the nitration of the alcohol is substantially complete.

In testimony whereof I affix my signature.

FRANK H. BERGEIM.

Patented Jan. 21, 1930

1,744,693

UNITED STATES PATENT OFFICE

FRANK H. BERGEIM, OF WOODBURY, NEW JERSEY, ASSIGNOR TO E. I. DU PONT DE NEMOURS & COMPANY, OF WILMINGTON, DELAWARE, A CORPORATION OF DELAWARE

DETONATOR

No Drawing.

Application filed May 3, 1928. Serial No. 274,966.

This invention relates to the production of an improved detonator. More particularly it relates to a composition blasting cap containing erythritol tetranitrate.

5 Blasting caps are ordinarily made by pressing a base charge into a metallic shell, and on top of this is pressed a priming charge with or without a capsule, depending upon the kind of primer used. Among the ex-
10 plosives which have been used as base charges are trinitrotoluene, tetryl, nitrated ivory nut meal, and smokeless powder. The most commonly used primers are mercury fulminate and lead azide.

15 While the above mentioned base charges have been used with a certain degree of success, it is desirable that they should possess a greater degree of sensitiveness to detonation by a primer, thus insuring regular performance, a matter of considerable importance in blasting practice. A shot that fails in blasting is a source of danger and expense.

20 An object of my invention is to provide a detonator that insures more regular performance than has hitherto been possible. Other objects will appear as the description proceeds.

25 I have found that desirable results can be obtained by incorporating erythritol tetranitrate into the cap composition. The erythritol tetranitrate may be incorporated in various ways. I may, for example, use any of the usual base charges in admixture with erythritol tetranitrate, or, if I desire a particularly powerful cap, I may use erythritol
35 tetranitrate as the sole base charge. I have found that a cap using erythritol tetranitrate alone as a base charge is more powerful than any of the commercial blasting caps now used. This great strength is of advantage
40 in insuring transmission of the cap explosion to the main bulk of blasting explosive. It has also an economic advantage in that it permits using smaller charges than can be
45 used successfully with the ordinary base charges. A further advantage obtained by using erythritol tetranitrate as a base charge is that successful caps can be made using
50 mercury fulminate without a capsule as a

primer. This effects a saving both in operation and materials.

In my U. S. Patent 1,691,954, dated Nov. 20, 1928, I have pointed out that erythritol tetranitrate has a melting point of 61° C. This low melting point makes this compound well adapted to casting and I have found that when cast this material can be detonated by means of a primary detonating compound such as mercury fulminate and in this form constitutes a very powerful detonating agent.

From the foregoing it will be seen that my invention is of wide application, and that, whereas I have confined my description of its use to blasting caps, it is understood that erythritol tetranitrate is equally well adapted to use in other detonating devices as, for example, booster charges for high explosive shells, which charges perform the same function with respect to the main charge in the shell as does the base charge in a blasting cap with respect to the dynamite.

The following are by way of illustration examples of blasting caps made in accordance with my invention: For a cap containing no inner capsule I may use a pressed base charge of erythritol tetranitrate ranging from 2 grains to 10 grains, depending on the strength of cap desired, with a superimposed charge of 8 grains of a 90-10 mixture of fulminate and chlorate. For a cap containing an inner capsule, I may use a base charge of 2 to 8 grains of erythritol tetranitrate with a top charge of 5 grains of 90-10 fulminate-chlorate mixture.

As many apparently widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that I do not intend to limit myself to the specific embodiments thereof except as indicated in the appended claims.

I claim:

1. A detonator having a main charge comprising erythritol tetranitrate.
2. A detonator comprising erythritol tetranitrate and a primary detonating compound.
3. A blasting cap having a main charge

comprising erythritol tetranitrate and a primer comprising fulminate of mercury.

4. A detonator having a main charge comprising cast erythritol tetranitrate.

5 5. A detonator comprising a base charge of cast erythritol tetranitrate and a top charge of a primary detonating compound.

6. A blasting cap comprising a base charge of cast erythritol tetranitrate and a priming
10 charge of fulminate of mercury.

In testimony whereof, I affix my signature.

FRANK H. BERGEIM.

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